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REVIEW OF EPA CONTRACT NO. 68-03-0497 ON SULFATE EMISSION CONTROL TECHNOLOGY

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REVIEW OF EPA CONTRACT NO. 68-03-0497 ON SULFATE EMISSION CONTROL TECHNOLOGY

by

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SECTION I

SUMMARY

Exxon has done excellent work on the assessment of automotive sulfate emission control technology, despite the many experimental difficulties involved in this type of work. The data produced have good reproducibility and are logically consistent between tests. The conclusions made by Exxon follow logically from the information compiled on their program and definitely appear correct to us. The Exxon conclusions on their four tasks are summarized below:

1.1 TASK I

Exxon assembled and examined literature pertaining to the fate of sulfur oxides in automotive exhaust systems. At temperatures above 400°C, decreasing the oxygen concentration decreases the equilibrium conversion. For example, operation at 0.2% oxygen instead of 5% could reduce the conversion by 25% to 65% over a typical oxidation catalyst temperature range of 500 to 650°C. However, from the thermodynamic standpoint, at lower temperatures (below 400°C), the absolute conversions of SO_2 to SO_3 could be as high as 70% at the 0.2% O_2 level. Due to kinetics, the conversion might not reach this level. Absolute control of sulfur trioxide production by control of excess oxygen concentration would be feasible at low temperatures only if the residence time were sufficiently short so that there was insufficient time to form SO_3.

A consideration of thermodynamics and kinetics indicate it is possible for sulfur trioxide formed on the catalyst to react with the substrate and exhaust system, only to be released later at a higher temperature as sulfur dioxide. This storage and release of sulfur compounds in the automobile exhaust system can play an important part in automobile sulfate emissions. Up to now there has not been enough information on this subject, owing to a lack of accurate analytical techniques and systematic study of the problem.

Exxon extensively reviewed the oxidation of SO_2 over platinum and platinum-alloy catalysts, but further review in the areas of catalyst poisoning and other industrial catalyst materials would be beneficial.

Based on another extensive review of the literature, Exxon concluded that calcium oxide appears to be the most promising sorbent for SO_3 if many engineering obstacles can be overcome.

1.2 TASK II

Exxon's work has confirmed the fact that sulfate emissions from non-catalyst-equipped, gasoline-fueled vehicles comprise less than 1% of the sulfur in the fuel. The conversion rate of sulfur to sulfate for diesels is slightly higher, averaging about 2%. However, diesels have substantially higher sulfate emissions than non-catalyst gasoline vehicles, due to the higher sulfur content of diesel fuel vs. gasoline.

1.3 TASK III

Among the many factors investigated by Exxon concerning the emission of sulfate from catalyst-equipped vehicles, the exhaust O_2 level and catalyst age were found to have

significant effects on sulfate emission rates. Sulfate emissions were substantially reduced by lowering the exhaust O_2 level. However, optimization of carburetion requires very close control of the air-fuel ratio, which requires special equipment such as the relatively-expensive electronic fuel injection system with feedback control from an O_2 sensor in the exhaust gas stream.

Exxon found that sulfate formation can be reduced by the use of aged catalyst without commensurate loss in control of CO and hydrocarbon emissions. With aged catalyst, the sulfate emissions were less than those from fresh catalyst by a factor of 50% or more. This suggests the possible future development of a new catalyst which would control CO and hydrocarbon with minimal sulfate production.

Exxon's finding that pelleted catalysts have a greater sulfate storage capacity than monolithic oxidation catalysts is of great interest. The sulfate stored by pelleted catalysts under urban low-speed (low converter temperature) operating conditions is released during the early stage of high-speed (high temperature) highway operation. Although the overall level of sulfate emissions in actual use may be the same for both pelleted and monolithic catalysts, the use of pelleted catalyst might lower the atmospheric sulfate level in urban areas. The impact of the storage and release phenomenon on the sulfate distribution and levels in the urban atmosphere is unknown for either catalyst. It might be possible, however, to make a design change to achieve maximum utilization of the storage and release mechanism to minimize the adverse impact of sulfate emissions in urban areas.

1.4 TASK IV

Despite extensive testing and a study of the feasibility of using solid sorbent traps for removal of sulfate from vehicle exhaust gas (or laboratory simulated gas), a satisfactory material has not been found which would meet all the necessary requirements for vehicle usage.

SECTION 2

MRC RECOMMENDATIONS

Based upon the results of this Exxon contract and our analysis of these results, we make the following recommendations:

(a) The concept of limiting the excess oxygen (e.g., 0.2% in exhaust gas) at a catalyst operating temperature range of 500 to 650°C is very promising. Further work is needed on the engineering development of this concept (such as use of feedback-controlled fuel injection system) for mass use. Such a system could reduce the conversion of SO_2 to SO_3 by 25% to 65%.

(b) Exxon's experimental finding that the sulfate emissions from aged catalysts were lower than those from fresh catalysts by a factor of 50% or more indicates the possibility of development of an automobile catalyst that can control CO and hydrocarbon with minimal sulfate production. This might be achieved with a new catalyst formulation (e.g., a different compound or loading) or by pre-treatment of fresh catalyst to reduce catalytic activity in the oxidation of SO_2 without a commensurate loss in CO and hydrocarbon control. This requires further extensive research and development.

(c) Exxon's experimental finding that pelleted catalysts definitely have a greater sulfate storage capacity

compared to a monolithic catalyst is of great interest. The sulfate stored by pelleted catalysts under urban low-speed operating conditions is released during the early stage of high-speed highway operating conditions. The impact of this finding on sulfate levels in urban atmosphere and health problems needs to be studied. Although the overall total amount of sulfate emissions in actual use may be the same for both catalysts, the distribution pattern of sulfate emission in or around the city may be quite different.

(d) If there is a definite advantage in using a pelleted catalyst for reducing urban atmospheric sulfate levels, then some changes in the size or location of the catalytic converter may be needed to achieve an optimum storage and release effect. The size and location of the converter, and the total loading of catalyst would influence and regulate the storage capacity, the operating converter temperature, and the storage and release mechanism.

(e) To gain an understanding of the storage and release mechanism of the catalyst substrate (i.e., Al_2O_3), further study of $Al_2(SO_4)_3$ decomposition in the presence of catalyst surfaces is needed. Exxon's laboratory-bench-scale study indicated that release of sulfate from $Al_2(SO_4)_3$ is not regulated by the SO_3/SO_2 equilibrium relationship, but rather by a hydrolysis mechanism.

(f) At this time further work to develop a sulfate trap is not warranted. This type of work is much less urgent than development of a good automobile oxidation catalyst system which has a minimum health impact.

(g) In view of the reconfirmation by Exxon of the very low sulfate emissions for gasoline vehicles without catalytic mufflers, work to minimize hydrocarbon emissions without their use appears to be another very worthwhile approach which should be pursued as a longer-range solution to the sulfate emission problem.

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16. ABSTRACT

The Monsanto Research Corporation reviewed the work performed by Exxon Research and Engineering under Environmental Protection Agency Contract No. 68-03-0497 and advised EPA on technical matters related to that contract. Based on this review of control technology for sulfuric acid emissions, the most promising way to control such emissions is to employ low exhaust oxygen levels. This control technique should be investigated further.

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SECTION 3

REVIEW OF EXXON'S FINAL REPORT

3.1 TASK I - LITERATURE SEARCH

Exxon assembled and examined the literature pertainting to the fate of sulfur oxides in automotive exhaust systems. The following subjects were examined and investigated from the literature:

- the thermodynamics of SO_3 formation, reaction with water, and condensation.
- the kinetics SO_3 formation and the fate of SO_2 and SO_3 in the exhaust system.
- the possible reaction of SO_3 with material in the exhaust gas or system.
- catalytic oxidation of SO_2 on Pt catalysts.
- possible means of removing SO_3 from the exhaust stream.

A possible control strategy emerged from the search. At temperatures above 400°C, decreasing the oxygen concentration decreases the equilibrium conversion. The rate-limiting step in the catalytic oxidation of sulfur dioxide is the surface reaction between adsorbed oxygen and adsorbed sulfur dioxide.

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The rate equation for industrial catalyst reported by Uyehara and Watson, appears also to be valid for automotive catalyst, indicating a possible control strategy of limiting the amount of oxygen over the catalyst. For instance, operation at a 0.2% oxygen concentration could reduce the conversion of SO_2 to SO_3 by 25% to 65% compared to that expected at 5% oxygen over the typical oxidation catalyst temperature range of 500 to 650°C. However, at the lower temperatures (<400°C), from a thermodynamic standpoint, absolute conversions of SO_2 to SO_3 could be as high as 70% at the 0.2% O_2 level. Therefore, absolute control of SO_3 production would not be feasible during low-speed (low temperature) operation.

Although good quantitative data are lacking, a consensus of the literature shows that the reaction rate is of sufficient magnitude that the oxidation of the exhaust SO_2 approaches equilibrium in actual vehicle operation. The extent of catalytic oxidation is somewhat clouded by problems of sulfur storage and inaccurate analytical techniques. The storage and release of sulfur oxides in the automobile exhaust system also can play an important part in automobile sulfate emissions. The thermodynamics and kinetics indicate that it would be possible for SO_3 formed on the catalyst to react with the substrate (e.g., aluminum oxide) and the exhaust system (ferric oxide), only to be released later at a higher temperature as SO_2.

Although Exxon extensively reviewed the oxidation of SO_2 over platinum and platinum-alloy catalysts, the area of catalyst poisoning was not covered. Loss in activity can result from chemical reactions between components in the exhaust gas stream and the catalyst surfaces. Another type of poisoning occurs as a result of physical coating or choking of the catalyst and the bed voids by foreign materials. As a matter

of fact, from Exxon's work on aged catalyst, it appears that a reduction of activity is beneficial in reducing sulfate emission, as long as there is no corresponding loss in CO and hydrocarbon emission control.

Other industrial (non-automotive) catalytic materials such as vanadium compounds, rhodium, platinum-rhodium, and oxides of iron, etc., have been shown to have catalytic activity in the oxidation of SO_2, but no references to them were included in the Exxon literature survey. In the February 1975 monthly report on this contract (EPA Contract No. 68-02-1320, Task 16) MRC summarized the results of a literature search made on catalyst poisoning and on noble metal catalysts used in the commercial manufacturing of sulfuric acid; hence, references on these subjects are available.

The literature has also been thoroughly reviewed by Exxon for the selection of the potential candidate sorbents to be used in a vehicle sulfate trap. The majority of references concern the selection of sorbent material for SO_2 removal from stack gases. However, since SO_3 is more reactive than SO_2, it would be expected that suitable SO_2 sorbents would also serve as suitable SO_3 sorbents. Considering the important factors of activity, thermal stability, volume and weight restrictions, potential side reactions, water solubility, cost, and toxicity, Exxon has concluded that calcium oxide appears to be the most promising sorbent for SO_3. Other possible sorbents are oxides of Mg, Mn, and Al.

3.2 TASK II - CHARACTERIZATION OF SULFUR EMISSIONS FROM NON-CATALYST VEHICLES

Task II involved measurement of SO_2, $SO_4^=$, and H_2S emissions from four non-catalyst vehicles:

- a 1974 350-cubic inch displacement Chevrolet V-8,
- a 1974 Mazda RX-4 equipped with a rotary engine,
- a 1974 Honda Civic equipped with a prechamber stratified charge engine,
- a 1975 Peugeot 504 GL equipped with a diesel engine.

Exxon's work confirmed the fact that sulfate emission from the non-catalyst equipped gasoline-fueled vehicles corresponds to less than 1% of the sulfur in the fuel. Conversion of fuel sulfur to sulfate is only slightly higher in the diesel vehicle, averaging nearly 2%. However, it should be noted that the sulfur values of diesel fuels (0.17 and 0.35 wt %) tested are about one order of magnitude higher than that of gasoline fuels. That means that diesel vehicles emit substantially higher sulfate than gasoline vehicles. It was assumed by Exxon that the presence of high amounts of carbonaceous particulate in the diesel exhaust may have caused a slight increase in the amount of oxidation of SO_2, either in the sampling or analytical procedure.

These low levels of conversion to sulfate found by Exxon in non-catalyst cars suggest that avoidance of the sulfate problem could be implemented if ways to achieve satisfactory levels of hydrocarbon emissions without catalytic converters could be developed. Though consistently achieving these levels without the use of catalysts will be difficult, avoiding the sulfate emissions problem and preventing the need for catalytic muffler installation and catalyst replacement seem to be sufficient incentive to seriously pursue this approach further, particularly as a longer range solution for these problems.

In tests performed by Exxon on all four vehicles, H_2S emissions were below the limit of detection of the Jacobs-Braverman-Hochheiser method (about 0.006 g/km).

At a low level of $SO_4^=$ emissions (approaching blank corrections) the absolute emission values reported by Exxon are less important than the fact that non-catalyst, gasoline-powered vehicles emit very little $SO_4^=$. The SO_2 values reported are somewhat erratic and invariably high due to early problems of interferences in using the TECO instrument, including quenching of the SO_2 fluorescence by O_2, CO, and CO_2, and spurious fluorescence by hydrocarbons. Exxon later calibrated the instrument in a background representative of the sample to be analyzed. The most out-of-line result was obtained with the Mazda, whose rotary engine put out the highest level of hydrocarbons. The SO_2 values collected by the H_2O_2 bubbler method show better reproducibility and accuracy (i.e., are closer to 100% sulfur balance), except at low levels of SO_2 from dilute exhaust.

Overall, Exxon has done commendable work in development and improvement of measurement techniques which are applicable to this particular task. These are discussed in section 3.5.

3.3 TASK III - FACTORS AFFECTING SULFATE EMISSION FROM OXIDATION CATALYST-EQUIPPED VEHICLES

3.3.1 Scope of Task III Work

Task III involved an assessment of the factors influencing conversion of SO_2 to SO_3 over commercial noble metal oxidation catalysts used for automobile emission control. Factors investigated by Exxon included:

- catalyst type (pelleted vs monolithic),
- noble metal composition (Pt vs Pt-Pd),
- noble metal loading (1.5 and 2.4 g/car, pelleted catalyst only),
- catalyst age (fresh vs aged with 0.0075 g/l lead for 4,000 km),
- exhaust O_2 level [without or with air pump (about 6% O_2)],
- catalyst temperature (450-650°C),
- residence time of exhaust gas over the catalyst.

Despite many experimental difficulties, Exxon studied those operating parameters of catalytic automotive emission control systems which might be adjusted to minimize sulfate emissions while maintaining CO and hydrocarbon control. Among the many factors investigated, the exhaust O_2 level and catalyst age were found to have the most significant effects on sulfate emission rates.

3.3.2 Discussion of Effects of Specific Parameters on Emissions

Lowering the exhaust O_2 level (as long as it is above 0.2%) shows definite promise as a means of simultaneously controlling CO, hydrocarbon, NO_x, and $SO_4^=$ emissions. Exxon's results indicate that by using an air pump only during cold engine operation, the sulfate emissions were lowered by a factor of 5 to 7 during the Federal Test Procedure tests and by factors of 2 (pelleted catalyst) and 10 (for monolithic

catalyst) at 96 km/h cruise. Optimization of carburetion requires very close control of the air-fuel ratio, such as might be achieved by an electronic fuel injection system with feedback control from an O_2 sensor in the exhaust gas stream. It is interesting to note that the sulfate emissions from this system are similar to those from a non-catalyst car. Further development work is required to demonstrate durable, low-cost, closed-loop fuel injection systems for catalyst-equipped vehicles. Today, very few cars are equipped with oxygen sensors. The Volvo, however, is equipped with a Bosch oxygen sensor and a three-way catalyst system which has shown low sulfate emissions under all test conditions.

However, if the exhaust is too rich, insufficient O_2 will be available to oxidize CO and hydrocarbon, and the level of these emissions will rise. If the exhaust is too lean, NO_x reduction, which does not proceed in the presence of excess O_2, will cease. It is not certain that production vehicles using an oxidation catalyst but without air pumps could meet the future, more stringent CO and hydrocarbon standards over extended operation periods.

Exxon found that aged catalysts were still adequate for the control of CO and hydrocarbon emissions, but their sulfate emissions were lower than those from catalysts by a factor of 50% or more. The fact that sulfate formation can be reduced without a commensurate loss in CO and hydrocarbon control, thus, suggests that it should be possible to develop a catalyst that can control CO and hydrocarbon with minimal sulfate production. Assessment of sulfate emissions from the total vehicle population based on sulfate measurement from fresh prototype cars would result in overestimation of the atmospheric sulfate levels. Further development of automotive oxidation catalysts with different catalyst compounds or

catalyst loading is needed. For example, the test results showed that Pt catalyst was more active than Pt-Pd catalyst for conversion of SO_2 to SO_3 and resulted in a magnification of the sulfate storage-release phenomenon.

Exxon found that pelleted catalyst definitely has a greater storage capacity for sulfate than the monolithic oxidation catalysts do, which is of great interest. Exxon's report shows that with pelleted catalyst only 23% of the sulfur in the gasoline was emitted in the exhaust during the low-speed Federal Test Procedure (FTP) runs, but that 158% was emitted at high-speed cruise conditions. In contrast, with monolithic catalyst, sulfur emissions averaged 92% of theoretical during the FTP and 135% during cruise conditions, showing less storage effect. The sulfate stored by pelleted catalyst under urban, low-speed (low temperature) operating conditions is released during the early stages (first 30 min) at high-speed (high temperature) highway operating conditions.

Although the overall level of sulfate emissions in actual use may be the same for both pelleted and monolithic catalysts, the use of pelleted catalyst might lower the atmospheric sulfate level in crowded metropolitan areas. The extent of the impact on the sulfate levels in urban atmosphere by using pelleted or monolithic catalysts is unknown at this time. Some design changes as to the size or location of catalyst converter may be needed to achieve an optimum storage-release mechanism for minimizing the health impact of sulfates released by automobiles having catalytic emission control systems.

It appears to us that decreasing the precious metal content per pellet of catalyst but using more pellets to retain the same total metal loading per converter should increase the

sulfate storage capacity. Locating the converter closer to the engine or to the tail pipe would influence the converter operating temperature, which in turn could influence both sulfate production and sulfate storage-release characteristics. New design configurations should be tested and optimized to control emission in urban areas.

In Appendix E of the Exxon report (Raw Data Table) it would have been beneficial to include catalytic converter operating temperature at each data point. Detailed temperature history might give further insight into the sulfate storage-release mechanism.

In relation to the sulfate storage-release effect, Exxon's laboratory bench scale study indicates that the initial release of sulfate from $Al_2(SO_4)_3$ is not regulated by the SO_3/SO_2 equilibrium relationship, but rather by a hydrolysis mechanism. Study of the decomposition in the presence of catalyst surfaces is needed to further understand the important sulfate storage-release phenomenon of automotive catalyst substrates.

In addition to the exhaust O_2 level and catalyst age, other factors investigated were: noble metal loading, catalyst type (pelleted vs monolithic), noble metal composition (Pt vs Pt-Pd), catalyst temperature, and residence time of exhaust gas over the catalyst. These other factors had less effect on total sulfate emission than exhaust or level or catalyst age, except under conditions where CO and hydrocarbon control also suffered.

In testing the *effect of catalyst noble metal composition,* platinum was found to be slightly more active than Pt-Pd for conversion of SO_2 to sulfate, especially at low-speed driving modes. This magnified the storage-release phenomenon with

The Pt catalyst and led to more storage on the catalyst with a resultant higher initial spike of sulfate emission at high speed (96 km/h). However, the subsequent sulfate emissions are comparable for both Pt and Pt-Pd catalysts. It is unknown whether Pt is really more active than Pt-Pd or whether this additional storage involves other unknown factors (e.g., types and quantities of substrate, manufacturing techniques, etc.) because the Pt and Pt-Pd catalysts were made by two different manufacturers.

In the study of the *effect of changes in catalyst operating temperature* on sulfate emissions, it is interesting to note that in most cases no significantly different results are obtained, even over ranges as large as 100°C. This is the only section in Exxon's report where catalyst operating temperatures were reported. Knowing the operating temperature for other data points would be of great interest. In the test, the pellet catalyst outlet temperature was raised (by insulating and heating) from 450 to 560°C for FTP, and from 620 to 730°C for 96 km/h cruise. In the test with the monolithic catalyst, the FTP operating temperature was decreased (by moving the converter toward the exhaust and cooling it) from 610 to 510°C while *cruise* temperature decreased from 645 to 540°C. A sharp drop in sulfate emissions was observed during the low temperature FTP runs, perhaps indicating a higher sulfate storage capacity at the lower operating temperature.

In testing the *effect of residence time*, the unexpected and perhaps important finding is that the sulfate emissions during the FTP test increased with increasing space velocity (i.e., short residence time), while sulfate emission decreased (also during the FTP test) with decreasing space velocity (i.e., long residence time). Results comparable with the base case were obtained during the 2-hour 96 km/h cruise runs by the

change in residence time. The seemingly anomalous findings are a strong indication of a sulfate storage effect at the low-temperature FTP operating conditions. Under the FTP conditions, sorption of sulfate on the catalyst substrate is the determining factor for sulfate emissions rather than kinetics of sulfate formation over the catalyst. Since sorption rate should increase with decreasing space velocity, then, under this assumption even though the rate of sulfate formation is increasing at lower space velocities, the rate of sorption increases even faster, resulting in a net decrease in tailpipe sulfate emissions. This also suggests possible engineering design changes for regulating urban atmospheric sulfate level by utilizing the sulfate storage-release mechanism, even though the overall total sulfate emissions remain the same.

To get a clear picture from the test results with catalyst-equipped vehicles, a typical sulfur balance and percent sulfur found as sulfate during the complete test cycle have been plotted, as shown in Figure 1, for both pelletized and monolithic catalyst-equipped cars. The figure shows that the FTP emissions of SO_4= were higher for the cars equipped with monolithic catalyst than for the car equipped with pelletized catalysts. The difference is even more pronounced for FTP #2. In both cases, SO_4= emissions for FTP #2 are much lower than for FTP #1 due to the apparent removal of stored sulfate during the preceding 2-hour high temperature cruise. Since the monolithic catalyst has a lower storage capacity than the pelletized catalyst, the monolithic catalyst allows more total sulfur oxides to escape during low temperature FTP and idle conditions than does the pelletized catalyst. Furthermore, at high temperature (96 km/h) conditions, the monolithic catalyst has much less stored sulfur oxides to give up, and approaches complete sulfur balance within the time span of the first half-hour measurement. In contrast, the pelletized

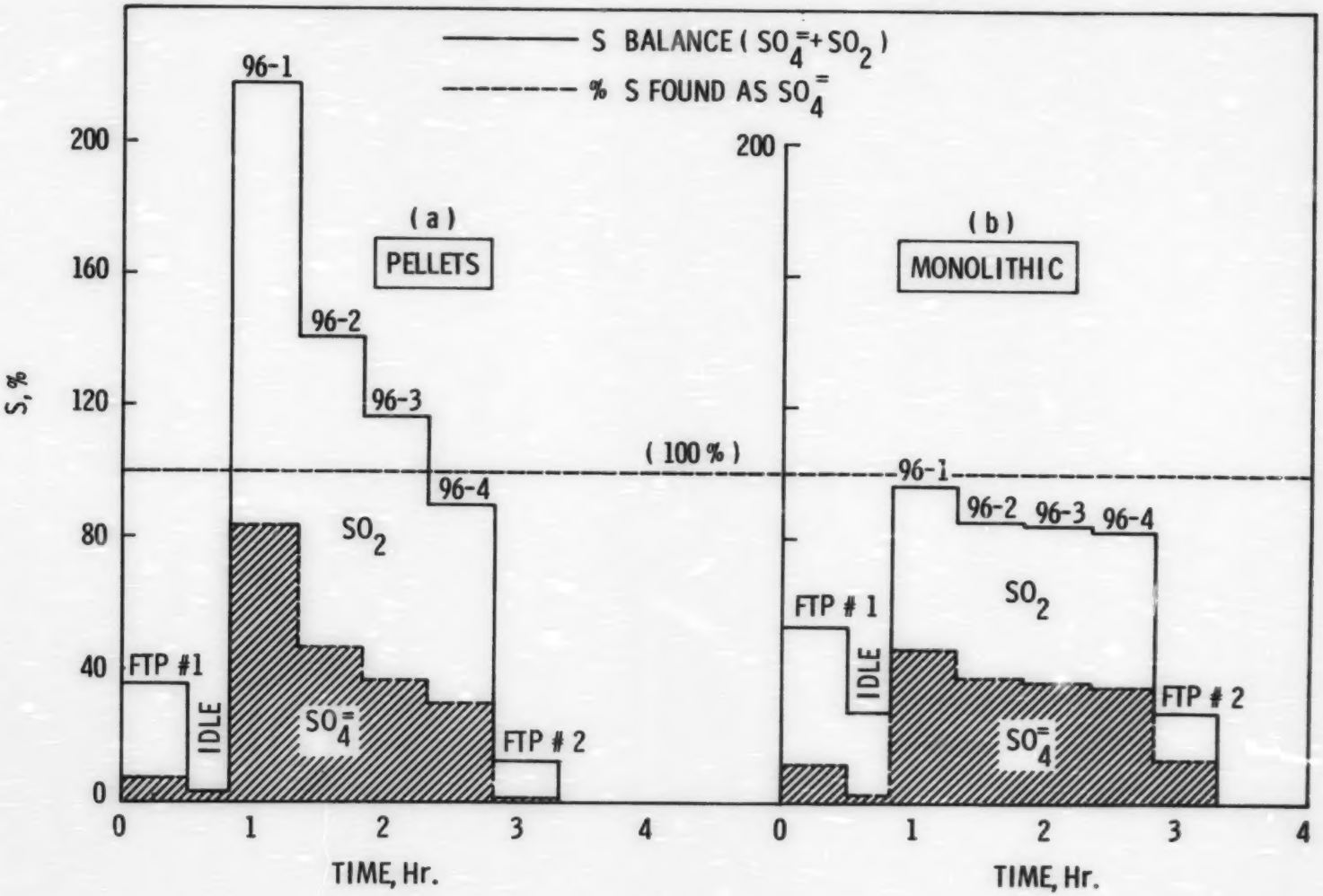

Figure 1. Typical comparisons of pellets and monoliths for sulfur oxides storage and $SO_4^=$ emissions.

catalyst requires at least 1-1/2 hours to reach the same condition. Although the monolithic catalyst emits more $SO_4^=$ during the FTP, this is counterbalanced by the emission of more $SO_4^=$ by the pelletized catalyst during the early stages of high speed cruise.

3.3.3 Summary of Results From Task III

To summarize the discussion presented above on the effect of catalyst and system operating variables on $SO_4^=$, the graphic representation of test results are reproduced from Exxon's final reports in Figures 2, 3, 4, and 5.

Figure 2 shows $SO_4^=$ emissions from pelleted catalysts during the first FTP cycle of the test sequence. It shows that the limited air Pt-Pd and aged Pt-Pd cases emit much less sulfate than the base case, while the short residence time significantly increases the emission of sulfate due to less storage effect (although there is less chance of oxidation with short residence time).

Figure 3 shows the average $SO_4^=$ emission from pelleted catalysts for the 2-hour, 96 km/h cruise. Overall emissions shown here are much higher than in Figure 2 for the FTP cycle. Again, emission of sulfate is least for the limited air Pt-Pd case.

Figure 4 shows $SO_4^=$ emission from monolithic catalysts during the first FTP. In comparing this chart with Figure 2, it is clear that the base case sulfate emission for the monolithic catalyst is much higher than that of the pelleted catalyst due to less storage effect during this low-temperature FTP cycle. Limited air Pt-Pd, three-way, and aged Pt-Pd catalysts emit less sulfate than other pelletized catalysts.

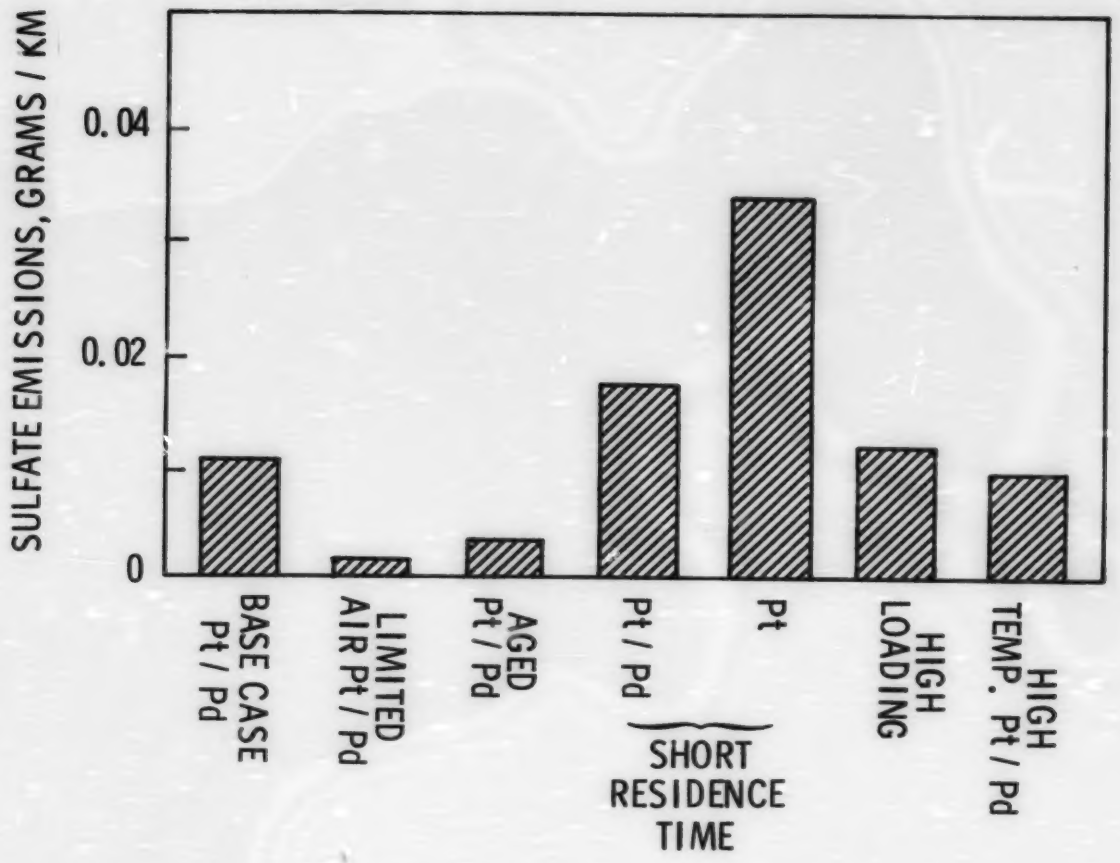

Figure 2. Effect of catalyst and system operating variables on sulfate emissions. Pelleted catalyst - FTP cycle.

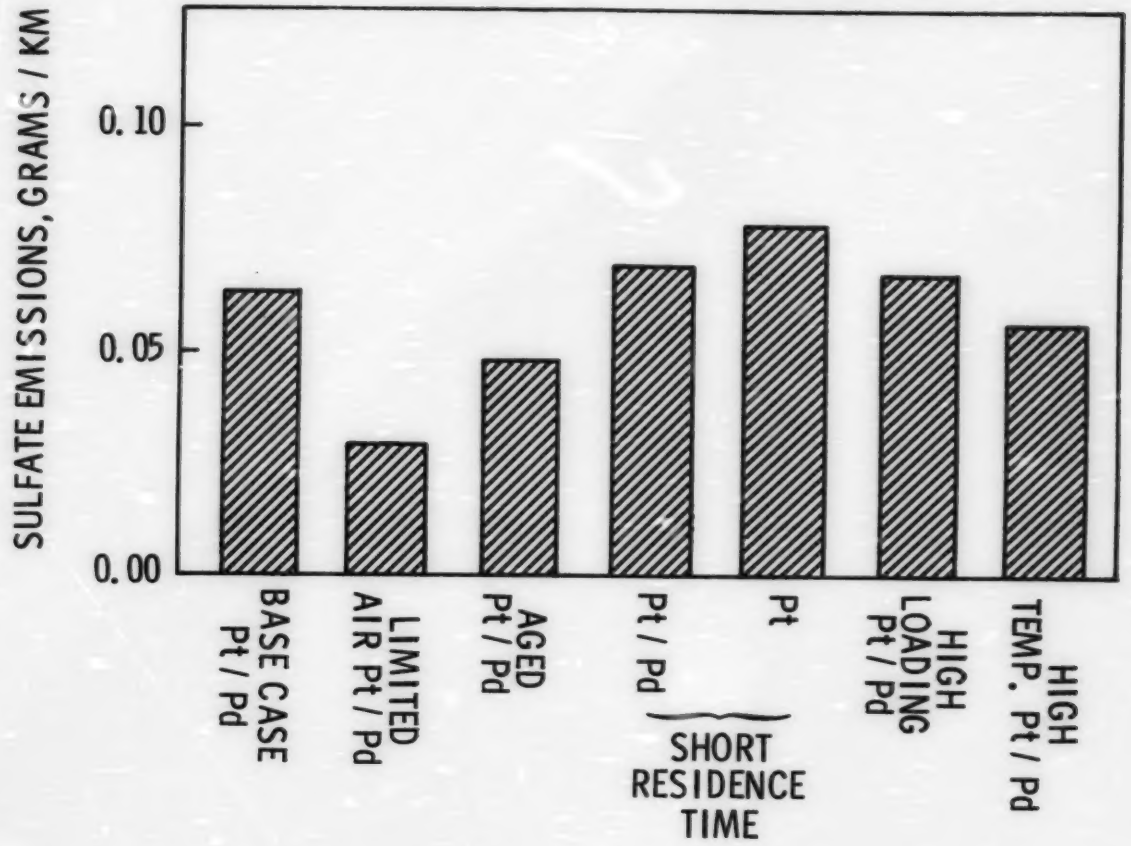

Figure 3. Effect of catalyst and system operating variables on sulfate emissions. Pelleted catalyst - 96 km/h cruise.

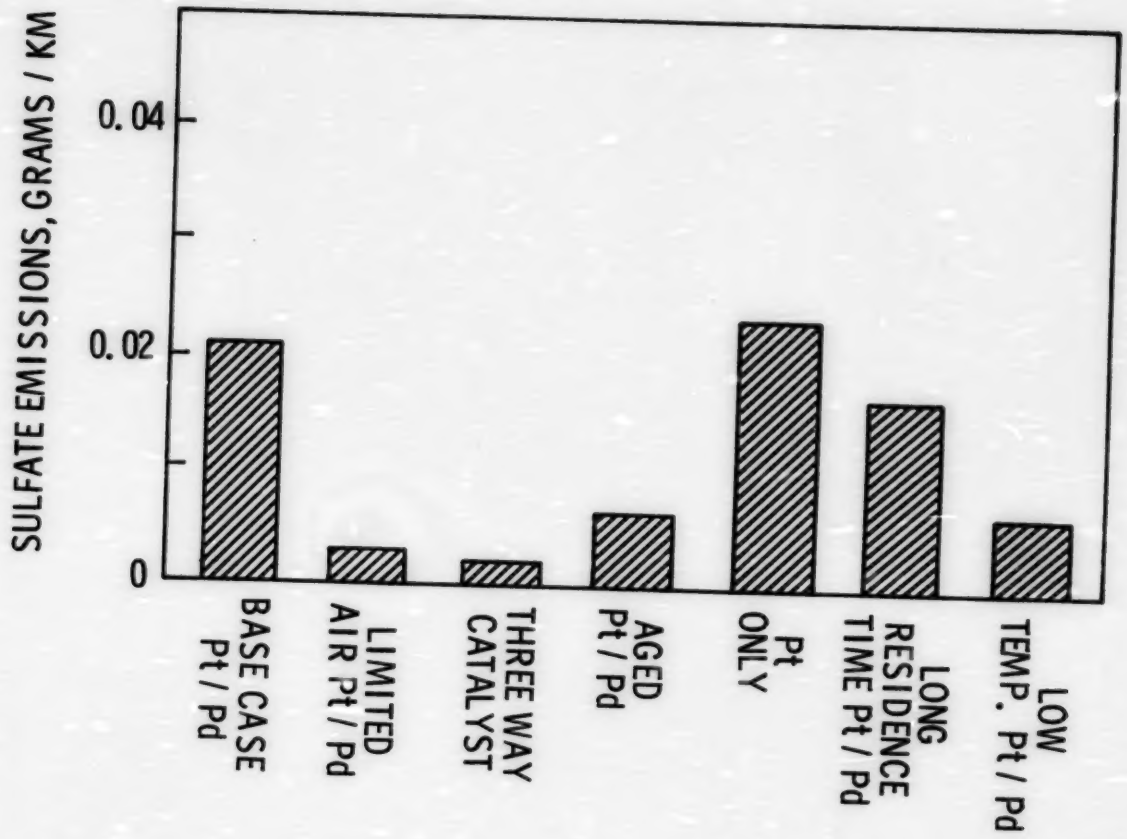

Figure 4. Effect of catalyst and system operating variables on sulfate emissions. Monolith catalyst - FTP cycle.

Figure 5 shows $SO_4^=$ emission from monolithic catalysts for a 2-hour, 96 km/h cruise. In contrast to the significant increase in sulfate emission for a short residence time during the FTP (Figure 2), doubling the residence time did not have much effect on sulfate emission with the monolithic catalyst during cruise conditions, indicating that the kinetics of sulfate formation are not an important factor.

3.4 TASK IV - FEASIBILITY STUDIES OF SULFATE REMOVAL FROM EXHAUST GAS BY TRAPS

It would be desirable to control the production of sulfate at the source rather than try to trap it after it has been produced. Exxon has done excellent work in a feasibility study of the use of a solid sorbent trap for removal of sulfate from the exhaust gas, both in vehicle tests and in laboratory screening. However, a satisfactory solid sulfate sorbent material which meets all of the necessary features needed for vehicle use has not been found.

The necessary requirements for potential sorbents are:

- active for SO_3 or SO_2 removal,
- thermally stable,
- not excessive in required total volume and weight,
- no potential side reactions, (e.g., carbonation, hydration),
- not water soluble,
- inexpensive and available,

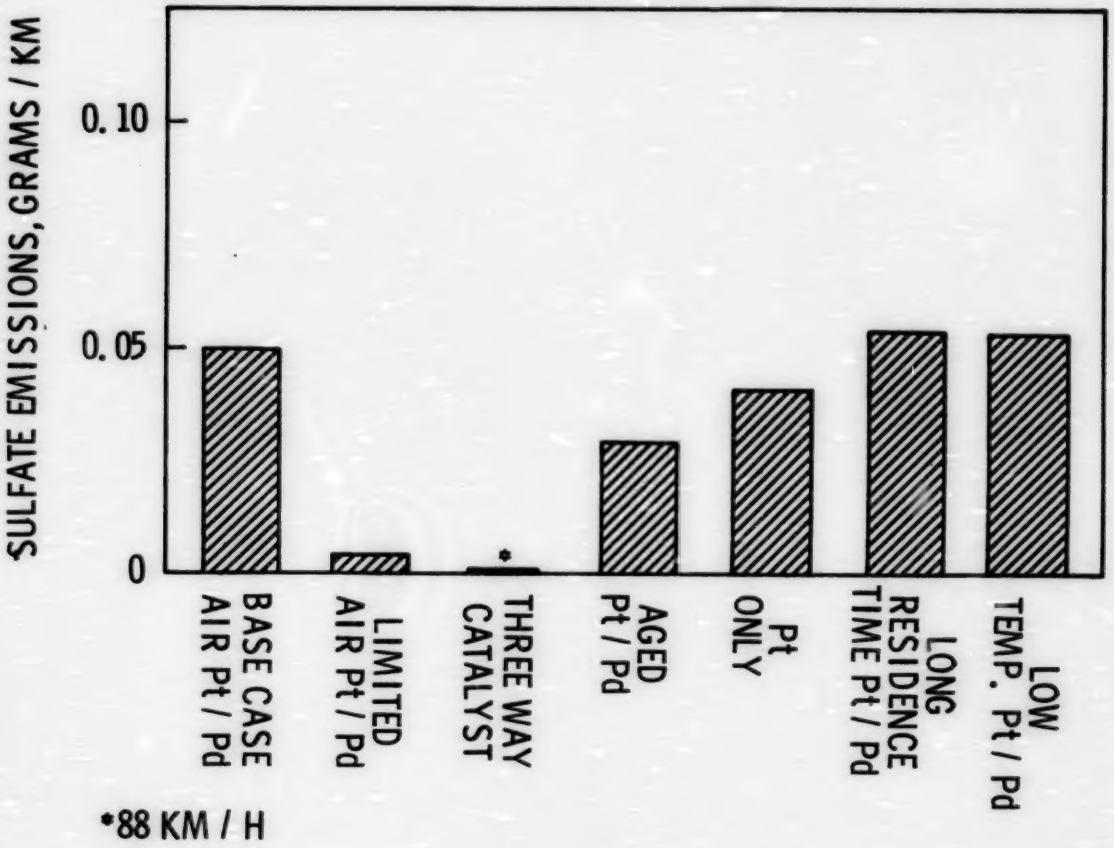

Figure 5. Effect of catalyst and system operating variables on sulfate emissions. Monolith catalyst - 96 km/h cruise.

•non-toxic, either fresh or sulfated.

At this time further work to develop a sulfate trap is not warranted. This type of work is much less urgent than development of a good automobile oxidation catalyst system which gives a minimum health impact as discussed in previous sections.

3.5 EXPERIMENTAL AND ANALYTICAL TECHNIQUES FOR THE MEASUREMENT OF SULFATE AND SO_2

Exxon used four basic analytical techniques for the measurement of sulfate and SO_2 emissions. These are listed in Table 1.

Table 1. CHARACTERISTICS OF ANALYTICAL METHODS

Species	Method	Exhaust Gas	Driving Modes	Sample Source
Sulfate	Filter	diluted	cyclic, constant speed	flowing gas
	Goksoyr-Ross	undiluted	constant speed	flowing gas
SO_2	TECO	diluted	cyclic, constant speed	flowing gas, bag
	Bubbler	undiluted	constant speed	flowing gas

Since there are two methods each for sulfate and SO_2 measurements, Exxon made a number of attempts to cross-check between them. Although some of these attempts did not yield agreement between the results, Exxon uncovered the reasons for this and described the limitations in the capabilities of these techniques under the operating conditions used.

Many of the difficulties found and overcome by Exxon throughout the entire contract period are worth noting. Sulfate emission samples were collected using Exxon's sophisticated exhaust

particulate sampling systems, and also by the Goksoyr-Ross technique. In order to function properly for sulfate emission measurement, it was necessary to make the particulate sampling system capable of:

- mixing the exhaust and diluent air rapidly,
- allowing development of a uniform velocity profile in the flow development tunnel,
- minimizing sampling losses in the tunnel,
- measuring equivalent emission rates with parallel filters, and
- maintaining constant temperature at the particulate collecting stage.

The sulfate content of samples collected by both methods was determined by colorometric titration using Sulfanazo (III) as an indicator. After experimental work identified sources of error, Exxon was able to eliminate errors and arrived at the following precautions about the titration procedure:

- add a minimum amount of HNO_3,
- keep water in the sample at a minimum,
- pH is very critical ($\sim$4.0),
- use blank for color comparison or end point,
- change Dowex resin frequently (after approximately 3 samples),

•if the sample is basic, adjust with nitric acid.

For example, for reliable results it was necessary to use a new batch of ion-exchange resin rather than a regenerated batch. Dowex ion exchanger resin must be changed frequently; large errors result if one attempts to work with a presumably regenerated ion exchange resin.

With the Goksoyr-Ross technique, Exxon found that, if metal sampling lines are to be used, only tubing which has been passivated by prior exposure to H_2SO_4-containing gases should be used to avoid possible reaction with sulfate. Otherwise, erroneous results may be obtained. Sulfation of the metal surface would lead to lower sulfate values, while the transfer of material (either entrained or vaporized acid, or actual chunks of metal sulfate flaked off the wall) would lead to high values.

The agreement obtained between the two different methods for sulfate determination was good, particularly near the end of the program. The early work to determine the levels of sulfate produced by noncatalyst cars probably contained the largest percentage error; however, since these levels were found to be low (1-2%), a relatively large percentage error in sulfate determination would not affect its absolute level significantly. The sulfate results and the conclusions which were based upon them should be valid.

SO_2 in diluted exhaust was measured using a Thermo-Electron Corporation (TECO Model 40) sulfur dioxide analyzer. SO_2 in raw exhaust was measured using a hydrogen peroxide bubbler method. At the beginning of Exxon's work on Task 2, the problems of the quenching effect of CO, CO_2, and O_2 on the fluorescence of UV-excited SO_2, and the interference due to

fluorescence of hydrocarbon compounds were not known. Nevertheless, the important finding is the fact that the sulfate emissions from the noncatalyst equipped vehicles are not significant, whether they represent 1 or 2% of the sulfur in the fuel. Later, Exxon calibrated the instrument in a background representative of the sample to be analyzed.

Another problem encountered with the TECO was that of sensitivity. In practice Exxon found the 0-10 ppm scale was too noisy to be used. It was necessary, therefore, to use the 0-50 ppm range. During the FTP driving cycle, SO_2 levels frequently dipped well below 1 ppm in the diluted exhaust gas, while at 96 km/h cruise the values were generally 2-3 ppm. Therefore, there was no way of knowing the "correct" value of SO_2 and the instrument did not appear useful for SO_2 concentration readings below several ppm.

Also, to eliminate the possibility of water adsorbing and condensing in the sample chamber on the walls and optical filters of the TECO instrument, Exxon initially used Drierite to remove the water, but it was found that at the 5-10 ppm level of SO_2 the Drierite removed all of the SO_2. The problem was solved by using the Permatube drying systems instead of Drierite.

With the peroxide bubbler method, Exxon found that both titrimetric and gravimetric techniques gave consistently high sulfur values, averaging 37% higher for titrimetric and 22% for the gravimetric method as compared to the theoretical value. Exxon reasoned that the most likely explanations for the higher values were errors caused by the difficulty of detecting the end point of the barium perchlorate-sulfanazo III titration or the need of blank correction. Subsequent to the end of the contract Exxon replaced the manual titration procedure with an automated system which included a

spectrophotometric end-point determination. This greatly reduced the blank corrections necessary. By comparing the 37% higher results for the titration method with the 22% higher results for the gravimetric method, it appears that the greater variability in manual titration results during the program did not markedly affect the SO_2 values calculated. The results reported and the conclusions drawn from them should still be valid.